

ELECTROCHEMICAL CHARACTERISTICS OF GRADED POROSITY CARBON ELECTRODES*

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INTRODUCTION

For the past several years Speer has conducted a comprehensive investigation of porous carbon electrode materials for use in fuel cells. Much of the information obtained from this study has been presented in various reports and papers (1-9). One result of this prior work has been the development of techniques for fabricating, from given formulations, carbon materials in which permeability and macropore distribution can be consistently and predictably varied over wide ranges.

A logical extension of this finding was to prepare carbon electrode materials which exhibit a pore size gradient across their thickness. By further refinements of the techniques, bodies have been fabricated which contain a pre-chosen number of layers of selected pore size distributions. The evenness of these strata and their mutual compatibility during processing is remarkable. To avoid extraneous variation, all layers of each sample are taken from the same formulation and, indeed, from the same basic mix.

The physical properties of these carbon electrodes and their electrochemical characteristics in fuel cell operation are presented below.

EXPERIMENTAL

Electrode Preparation

A formulation of petroleum coke and coal tar pitch was selected for the initial fabrication of these novel materials. A lignon sulfate derivative marketed under the trade name Orzan was used as an additive. The latter is employed as a means of increasing the porosity of the baked carbon through exfoilation during the baking process. The materials were intimately mixed at 135°C. and then crushed to desired size when cooled. The sized materials were then placed in very even layers in a molding die in the chosen sequence and thickness. All samples were

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then molded and baked under uniform conditions to yield electrodes of two of three zones of predictable permeability and macropore distribution. The physical properties of these samples are given in Table I.

Samples 1-Pt through 3-Pt were fabricated in similar fashion except that 2 mg of platinum black per square centimeter of geometrical surface were added to the zone marked with an asterisk. These materials were processed under conditions identical to the first set.

Samples 1-Ch through 3-Ch of Table I were identical to Samples 1 through 12 except for substitution of a hardwood charcoal for the petroleum coke used as the filler material in order to obtain very porous, hydrophillic materials. The contact angle with water, given in Table I, is a measure of the hydrophillic, i. e., wetting, character of the material; the lower the angle the more hydrophillic the material. It is readily seen that the charcoal materials are both quite porous and hydrophillic.

Electrochemical Evaluation

Polarization characteristics of carbon electrodes have been determined with the laboratory hydrogen-oxygen fuel cell previously described (10). The entire system was reduced to thermal equilibrium at $25.0 \pm 0.2^\circ\text{C}$. prior to measuring the electrode polarization in order to remove temperature dependent processes from consideration. Sulfuric acid (3.0 N) was employed as the electrolyte. The electrode preparation procedure was varied only in the application of wetproofing where desired. Some electrodes were wetproofed by treating with a solution of 2 g. paraffin per 100 ml petroleum ether (b. p. range $30-60^\circ\text{C}$.) and allowed to dry in air. This was normally followed by catalyzing with 2 mg. platinum black per square centimeter of geometrical surface area as recommended by Taschek (11). Where no wetproofing was applied, the pre-treatment proceeded directly to the catalyzing step. No activation of electrode materials was employed so that the possibility of masking the effects and interactions of electrode process variables, raw materials, etc., could be obviated. The electrodes were studied with a one-inch by one-inch surface in contact with the aqueous electrolyte.

A modified Kordes-Marko bridge circuit (12) was constructed for interrupting the current during measurement of the electrode potential. This bridge circuit provides for the measurement of combined polarization due to activation and concentration by eliminating the influence of resistance polarization.

DISCUSSION OF RESULTS

Gas Pressure Studies

The pressures of hydrogen and oxygen were varied so that the electrical output could be determined as a function of gas pressure. The maximum pressure used was just less than that needed to cause rapid continuous gas bubbling from the surface of the electrode. The maximum pressure varied with the particular surface facing the electrolyte and the gas involved. In this work that quantity has been termed the "bubble pressure". The description of the porosity gradients for the materials studied is summarized in Table I which shows that a variety of two- and three-layered materials have been prepared. Some have a very coarse zone on one face which de-

TABLE I
Properties of Graded Porosity Electrode
Materials

Sample	Thickness (inches) of			Permeability (darcys)			Probable Pore Diameter Range (in microns, μ)			Contact Angle ($^{\circ}$)			Surface Area (m^2/g)		
	Zone			Zone			Zone			Zone			Zone		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
1	0.031	0.031	0.031	1.38	0.45	0.14	9->90	5-25	3-7	77.0	32.5	28.0	37.4	56.7	137.7
2	0.031	0.031	0.031	1.38	0.45	0.05	9->90	5-25	3-4	77.0	32.5	27.0	37.4	56.7	158.2
3	0.125	0.031	--	1.38	0.14	--	9->90	3-7	--	77.0	28.0	--	37.4	137.7	--
4	0.125	0.031	--	1.38	0.05	--	9->90	3-4	--	77.0	27.0	--	37.4	158.2	--
5	0.031	0.031	0.031	1.38	1.16	0.76	9->90	8-40	8-20	77.0	79.5	30.0	37.4	71.0	43.3
6	0.031	0.031	0.031	0.24	0.14	0.09	6-14	3-7	3-6	34.5	28.0	39.0	46.5	137.7	181.0
7	0.031	0.031	0.031	1.38	0.76	0.14	9->90	8-20	3-7	77.0	30.0	28.0	37.4	43.3	137.7
8	0.031	0.031	0.031	1.38	0.76	0.05	9->90	8-20	3-4	77.0	30.0	77.0	37.4	43.3	158.2
9	0.031	0.031	0.031	1.38	0.05	1.38	9->90	3-4	9->90	77.0	27.0	77.0	37.4	158.2	37.4
10	0.031	0.031	0.031	0.05	1.38	0.05	3-4	9->90	3-4	27.0	77.0	27.0	158.2	37.4	158.2
11	0.031	0.031	0.031	1.38	0.45	0.33	9->90	5-25	3-5	77.0	32.5	37.5	37.4	56.7	129.3
12	0.125	0.031	--	1.38	0.33	--	9->90	3-5	--	77.0	37.5	--	37.4	129.3	--
1-Pt	0.031*	0.031	0.031	1.38*	0.45	0.14	9->90*	5-25	3-7	77.0*	32.5	28.0	37.4*	56.7	137.7
2-Pt	0.031	0.031*	0.031	1.38	0.45*	0.14	9->90	5-25*	3-7	77.0	32.5*	28.0	37.4	56.7*	137.7
3-Pt	0.031	0.031	0.031*	1.38	0.45	0.14*	9->90	5-25	3-7*	77.0	32.5	28.0*	37.4	56.7	137.7*
1-Ch	0.031	0.031	0.031	0.26	0.35	0.24	1.5-20	1-7	0.9-6	41.5	11.0	16.0	--	--	--
2-Ch	0.031	0.031	0.031	0.24	0.27	0.26	0.9-6	0.9-6	0.9-6	16.0	35.0	27.0	--	--	--
3-Ch	0.031	0.031	0.031	0.26	0.23	0.35	0.9-6	0.9-5	1-6	27.0	26.0	25.0	--	--	--

creases to a finer zone on the opposite face; some are "uniformly coarse" or "uniformly fine"; and some have a coarse zone sandwiched between two fine zones or vice versa. Each material was evaluated with both the "fine" (F) and the "coarse" (C) side facing the electrolyte. The first six materials listed in Table I were also tested in the experimental fuel cell in both a wetproofed (WP) and non-wetproofed (NWP) condition. The next twelve materials were tested only in the non-wetproofed condition.

The observed current density at 0.3 volt polarization and the bubble pressure appear to vary with the surface facing the electrolyte and the application of wetproofing to the electrode material. These data are summarized in Table II for the samples 1 through 12. In a non-wetproofed condition, the graded electrodes usually yield a higher current density at a lower fuel gas pressure when the finer porosity zone faces the electrolyte. In all but one case (Sample 6), it is seen that better performance is attained when the materials are not wetproofed. Even in Sample 6 the non-wetproofed fine zone yields higher current densities on the fine side. This could be interpreted as evidence of increased available active carbon surface together with improved catalyst proximity to this active surface. Sample 6 is the most "uniformly fine" material (or perhaps most like a standard, non-graded electrode) and in this case wetproofing due to paraffin was found to be beneficial.

Another possibility is that the wetproofing treatment inhibits the total contact of catalyst with the electrode and electrolyte due to the fact that part of the catalyzing treatment involves a reheating of the electrode to a temperature well above the melting point of the hydrophobic agent (paraffin). During the heat treatment, while the paraffin is molten, it is probable that a fraction of the catalyst is also wetproofed. If this occurs, then the wetproofed, catalyzed electrode can be regarded as less active than a non-wetproofed, catalyzed electrode and may even result in a somewhat different electrochemical response. To test this hypothesis the following series of experiments were performed: A series of 5 mm carbon discs from the same bulk sample and prepared from identical materials as the graded porosity electrodes were sealed into the end of a glass tube. An electrical contact was made on the inside of the tube to the surface of the carbon. The tube was connected to a source of oxygen and placed into a 3 N sulfuric acid solution as part of a conventional polarographic system in which the carbon discs were the working electrodes. Oxygen pressure was then applied so that a bubble of oxygen was allowed to escape from the carbon disc into the solution at a rate no greater than once every 5 seconds. The potential was then scanned in a cathodic direction using a Sargent Model XXI Recording Polarograph over the range +0.3 to -1.2 v vs S.C.E. Four different electrodes were used: (1) an untreated carbon electrode, (2) a catalyzed but non-wetproofed electrode, (3) a catalyzed and wetproofed electrode and (4) an electrode which was only wetproofed. The first material gave $E_{1/2}$ values which corresponded to the reduction of oxygen to peroxide and the reduction of peroxide to hydroxide. The second material was so active that the size of the disc had to be cut down to 2 mm diameter in order to hold the current response on scale for the same two reductions. Electrode No. 3 gave only a poorly defined response for the second reduction, the first being entirely absent. The last material showed hydrogen evolution as the only electrode reaction. The presence of the wetproofing material inhibited the polarographic response, in probably the same manner in which the fuel cell process is retarded. Wetproofing is thus to be detrimental to optimum electrochemical performance. However, some exceptions to this behavior have been noted, as was seen for Sample 6, above, where the wetproofed sample showed a better electrochemical

TABLE II
Current Density at 0.3 v Polarization and Bubble Pressure as
a Function of Wetproofing and Porosity of Electrode Surface

Sample*	Wetproofed				Non-Wetproofed			
	Current Density (ma/cm ²)		Pressure +		Current Density (ma/cm ²)		Pressure +	
	H ₂	O ₂	H ₂	O ₂	H ₂	O ₂	H ₂	O ₂
1F	17.3	31.0	25.8	26.7	28.5	50	37.6	19.7
1C	12.8	13.5	2.1	7.3	23.0	29.5	1.6	1.4
2F	4.4	8.2	103.3	98.1	28.0	70	1.6	99.5
2C	7.3	3.9	101.1	95.7	12.2	18.9	16.3	1.7
3F	1.66	0.93	96.2	97.5	8.4	20	26.7	26.0
3C	15.5	10.00	1.9	48.2	11.8	9.5	1.4	1.1
4F	2.40	1.37	6.3	98.7	9.9	4.6	71.6	73.3
4C	2.75	0.61	3.1	1.7	3.8	1.0	52.4	47.0
5F	2.1	2.24	2.90	37.4	12.5	3.1	55.5	37.5
5C	2.9	0.76	30.0	1.1	5.4	1.3	33.6	32.6
6F	44.0	70	54.1	81.8	9.4	15	31.9	48.3
6C	29.8	1.11	1.6	35.1	15.4	3.35	47.0	2.4
7F					16.0	0.6	78.4	70.0
7C					9.2	2.9	67.0	53.5
8F					--	0.7	58.0	41.5
8C					15.0	1.0	68.8	50.8
9C					11.3	1.2	95.8	71.7
10F					22.0	21.0	31.2	30.9
11F					23.0	14.1	31.0	26.5
11C					17.0	5.8	80.3	84.5
12F					13.5	2.3	40.0	46.2
12C								

*F indicates fine side facing electrolyte, C coarse side; See Table I

+in cm. of dibutyl phthalate

response. In all other samples wetproofing has a definite inhibiting effect on electrochemical performance. Because of this, it was decided to omit the wetproofing step from the evaluation of all remaining graded porosity electrode materials.

One interesting interpretation of these results can be made by utilizing the capillary transport theory proposed by Hunger (13). It is postulated that the force (i. e., pressure, p) needed to move the gas through a wetproofed capillary (i. e., pore) can be expressed as a function of the radius (r) of the pore, the surface tension (γ) of the electrolyte and the contact angle (Θ) of the meniscus formed between the electrolyte and the porous body. This relationship is expressed by a form of the Washburn equation (14)

$$p = \frac{2\gamma \cos \Theta}{r} \quad (1)$$

When " p " is the maximum pressure which can be applied to the porous body while still maintaining some electrolyte within the capillary, i. e., the bubble pressure, then a limiting value of the pore radius, r , can be calculated for a particular carbon electrode material. The results of such a series of calculations for the first twelve graded porosity materials listed in Table I are given in Table III. A comparison of these calculated pore radii with predicted pore diameter range presented in Table I leads to some interesting conclusions. It is apparent, from the comparison of the predicted and calculated pore sizes that the position of the reaction interface, i. e., the common point in the interior of the electrode material where the gas, electrolyte and electrode meet, varies from one electrode material to another. In some cases the electrolyte apparently diffuses well into the body of the electrode material as is shown by materials 1-WP, 2-WP, 3-WP, 6-WP and 1-NWP in which the calculated limiting pore radii appears not to be in the zone facing the electrolyte, but, rather into the middle or opposite outer zone. In most cases it is also apparent that the reaction interface is not on the apparent surface of electrode material but well within the body of the electrode. For the non-wetproofed materials it is interesting to note that the calculated limiting pore radii are smaller when the finer zone faces the electrolyte than when the coarser zone is in the reacting position. This is true for all the materials save Sample 1 which shows the opposite effect. When the materials are wetproofed, however, it would appear that the paraffin tends to close some of the smaller pores on the finer zone as most of the calculated limiting pore radii are larger than, or about the same magnitude as, the values obtained for the coarser zone. For those materials which have not been wetproofed the position of the reaction interface depends on the material. Referring to Table III, it is apparent that when the fine zone of Sample 1 is facing the electrolyte the limiting pore radius is 15.35 μ indicating that the reaction interface is at least in the middle zone or at the interface between the coarser and middle zone. When the coarser side faces the electrolyte the limiting pore radius decreases to an extent that the reaction interface must be in the fine zone. Thus the electrolyte appears to diffuse through two zones into the finer zone to react with the fuel gas. For Sample 1, when the coarse zone faces the electrolyte, the presence or absence of a hydrophobic paraffin coating makes little difference with respect to the position of the reaction interface. Apparently, the interface location is a function of the diffusability of both the fuel gas and the electrolyte, as well as the factors given in Equation 1. In the case of Sample 2 the untreated material is easily wet by the electrolyte as evidenced by the low contact angles ($F-28^\circ$, $C-77^\circ$). When the material possesses a hydrophobic film on the surface, however,

TABLE III
Electron Change (Δn) Values and Calculated Limiting Pore Radii
for the Oxygen Electrode

Sample*	Limiting	Bubble	E_o		O.C.V.	
	Pore Radius μ	Pressure, atm.	at 1 atm vs NHE	Δn^+	H ₂	O ₂
1-F-WP	5.56	0.0730	--	NNB	-0.026	0.886
1-C-WP	4.17	0.0975	0.797	3.38	-0.043	0.816
2-F-WP	5.45	0.0745	0.810	2.27	-0.034	0.905
2-C-WP	4.18	0.0970	--	--	-0.039	0.770
3-F-WP	4.12	0.0985	--	NNB	-0.028	0.878
3-C-WP	4.10	0.0900	--	NNB	-0.046	0.666
4-F-WP	4.06	0.1000	0.785	0.83	-0.039	0.859
4-C-WP	21.20	0.0191	0.782	3.48	-0.031	0.811
5-F-WP	8.08	0.0502	0.808	2.27	-0.022	0.842
5-C-WP	14.00	0.0290	--	NNB	-0.023	0.869
6-F-WP	8.60	0.0471	0.832	0.75	-0.014	0.855
6-C-WP	4.93	0.0825	0.786	2.82	-0.016	0.889
1-F-NWP	15.35	0.0199	0.737	2.20	-0.017	0.857
1-C-NWP	3.41	0.0972	0.843	4.18	-0.035	0.845
2-F-NWP	1.30	0.1005	0.817	2.56	-0.020	0.929
2-C-NWP	9.18	0.0360	0.765	1.42	-0.018	0.827
3-F-NWP	2.76	0.0354	--	NNB	-0.017	0.944
3-C-NWP	6.33	0.0523	--	NNB	-0.034	0.904
4-F-NWP	1.76	0.0740	0.832	3.87	-0.027	0.928
4-C-NWP	6.85	0.0480	--	NNB	-0.042	0.939
5-F-NWP	3.32	0.0380	0.970	0.94	-0.040	0.879
5-C-NWP	9.95	0.0333	1.025	0.89	-0.025	0.939
6-F-NWP	1.77	0.0645	--	NNB	-0.016	0.897
6-C-NWP	20.60	0.0248	0.730	1.42	-0.017	0.859
7-F-NWP	5.50	0.0707	0.772	1.59	-0.019	0.934
7-C-NWP						
8-F-NWP	2.40	0.0540	--	NNB	-0.021	0.976
8-C-NWP	7.83	0.0420	0.793	2.60	-0.027	0.947
9-C-NWP	6.40	0.0515	0.985	0.76	-0.020	0.900
10-F-NWP	1.79	0.0725	0.887	0.92	-0.011	0.811
11-F-NWP	3.72	0.0311	0.789	4.20	-0.019	0.769
11-C-NWP	12.26	0.0268	--	NNB	-0.026	0.781
12-F-NWP	1.36	0.0855	0.929	0.77	-0.008	0.848
12-C-NWP	7.00	0.0468	--	NNB	-0.030	0.845

*F signifies fine side facing electrolyte; C coarse side, See Table I

Average $E_o = 0.832$ vs N.H.E.

[†]NNB = Non Nernstian behavior

there appears to be deeper penetration of the electrolyte from the fine side than when this film is absent. The small limiting pore radius of 1.30μ is well within the $3-4\mu$ diameter range expected for the unwetproofed fine zone of Sample 2. This low limiting pore radius indicates that the reaction interface is apparently at or just under the geometrical surface, in the fine zone. Apparently, the hydrophobic film present in wetproofed materials is not the only controlling factor influencing the diffusion of the electrolyte and the position of the reaction interface. Sample 6 gives a very unusual limiting pore radii for both its fine and coarse zones. When the fine zone faces the electrolyte it is quite apparent that the reaction interface can only be in the fine zone. When the coarse zone faces the electrolyte the calculated limiting pore radius is larger than the pores expected to be present in the material. Either the reaction is occurring at the "real surface" of the electrode or the material has developed unusually large and unexpected pores during fabrication. Samples 7 through 12 show limiting pore radii which are consistent with the pore size of the zone facing the electrolyte. Because Samples 9 and 10 are made up of a fine zone sandwiched between two identical coarse zones and a coarse zone sandwiched between two identical fine zones, respectively, it is impossible to determine which zone contains the reaction interface.

It has been suggested (15) that the concentration of the catalyst in a preferential location within the body of the material may influence the observed variation of the position of the limiting pore radius. To test this possibility, a series of materials duplicating Sample 1 were prepared in which 2 mg. of platinum black per square centimeter of geometrical surface area was added to one zone per sample. These materials were then examined in the fuel cell in the same manner as the other graded porosity materials. If the location of the catalyst exerts a preferential effect then the calculated limiting pore radius should be in the range of the zone which contains the catalyst. Sample 1 was chosen because its three zones represent a coarse, medium and fine porosity. The results of this study are summarized on Table IV in which Sample 1-Pt contains the catalyst in the coarse zone, Sample 2-Pt contains the catalyst in the middle zone and Sample 3-Pt has the catalyst in the fine zone. The results are, at best, inconclusive as to the relationship between limiting pore radius and catalyst position. Sample 1-Pt definitely shows that the limiting pore radius and thus the reaction interface is not in the fine zone, regardless of which side faces the electrolyte. However, the values obtained for the limiting radius leave considerable doubt as to whether the reaction interface is in the coarse (outside) or middle zone. For Samples 2-Pt and 3-Pt the location of the reaction interface appears to depend on which side of the electrode is facing the electrolyte. The values obtained for the limiting pore radius suggest that the reaction interface appears to be located in the zone facing the electrolyte. If diffusion into the bulk of the electrode material does occur, then these calculated radius values strongly suggest that the deepest electrolyte penetration is only into the middle zone. A similar conclusion can be obtained by inspection of the limiting pore radii given for the non-wetproofed samples in Table III.

The presence of a foreign hydrophobic material like paraffin apparently alters the physical as well as the electrochemical nature of the electrode material by filling up the smaller pores as well as covering the entire material with a fine film. In this respect, it is interesting to note that the bubble pressures are usually higher for a given material when it has been treated with paraffin. This can be explained if it is assumed that the wetproofing treatment tends to fill the smaller pores,

reduce the diameter of the larger pores and, perhaps, reduce the number of complete routes through the material in which a gas and/or electrolyte can flow.

Two standard, single-layered electrode materials made from the same raw materials as the graded porosity electrodes were also run at varying gas pressures. These results are given in Table V. Both these materials were wet-proofed before testing. It is seen that the finer material has the larger limiting pore radius, indicating that some of the smaller pores were filled with paraffin. These data are admittedly limited but it is interesting to note, as described in greater detail below, that the electron change values correspond to a peroxide or hydroperoxide mechanism at the reaction interface. This corresponds rather well with the assumed change using the layered, graded porosity materials described above.

TABLE IV
Electron Change (Δn) Values and Calculated Limiting Pore Radii for the
Oxygen Electrode at Platinum Loaded Materials

Sample	Limiting Pore Radius, μ	Bubble Pressure, atm.	E_0 at 1 atm vs N. H. E.	Δn	Open Circuit Voltage at Bubble Pressure	
					H_2	O_2
1-Pt-F	5.30	0.0242	0.857	3.50	-0.191	0.831
1-Pt-C	7.06	0.0465	1.042	1.26	-0.179	0.944
2-Pt-F	3.76	0.0345	1.015	3.75	-0.062	0.002
2-Pt-C	12.00	0.0273	1.000	2.15	-0.196	0.961
3-Pt-F	3.13	0.0413	0.962	2.73	-0.139	0.934
3-Pt-C	17.00	0.0193	1.070	2.64	-0.206	0.916

Average $E_0 = 0.991$ v vs N. H. E.

The open circuit voltages (O. C. V.) of the materials listed in Tables III, IV, and V provided some intriguing results. For the materials in Table III it is noted that generally the non-wetproofed materials have a higher O. C. V. than the wetproofed materials. Also, it is apparent that when the finer zone of a given electrode faces the electrolyte a higher O. C. V. is obtained regardless of the presence or absence of a hydrophobic agent. There are some exceptions to this, as for example Sample 5, but these occur in the materials in which the graded porosity is less extreme. The addition of platinum to the various layers during fabrication appears to enhance the values of the open circuit voltages. While the data in Table V is limited, the trend with respect to the fine-coarse-open circuit voltage relationship is consistent with that of the other materials.

Table VI lists the electrochemical performance of the charcoal materials. Unlike the former materials, charcoal based carbons are easily "wet" by aqueous solutions. Thus the limiting pore radius at the bubble pressure indicates a large amount of diffusion within the electrode by the electrolyte. The bubble pressures are all very low indicating the probable existence of a large number of continuous pores through the material.

TABLE V
Properties and Electrochemical Performance of Standard
Electrodes

Sample	13	14*
Permeability (darcys)	0.285	0.366
Probable Pore Diameter (μ)	2-9	1.5-9
Calculated Limiting Pore Radius (μ)	3.60	2.22
Bubble Pressure (atm.)		
H ₂	0.0395	0.0520
O ₂	0.0350	0.0550
E ₀ at 1 atm. (vs N.H.E.)	0.840	0.892
Δn	1.8	2.5
Open Circuit Voltage		
H ₂	-0.017	-0.016
O ₂	0.859	0.782

- * Basal planes of crystallites in this sample orientated perpendicular to surface of material; other sample orientation is parallel.

TABLE VI
Electron Change (Δn) Values and Calculated Limiting Pore Radii
for the Oxygen Electrode at Charcoal Materials

Sample	Limiting Pore Radius, (μ)	Bubble Pressure atm.	E ₀ at 1 atm vs N.H.E.	Δn^+	Open Circuit Voltage at Bubble Pressure	
					H ₂	O ₂
1-Ch-C	4.92	0.0222	0.740	1.65	-0.022	0.799
1-Ch-F	10.01	0.0141	0.595	1.45	0.043	0.699
2-Ch-C	3.81	0.0370	0.727	3.87	-0.019	0.749
2-Ch-F	7.65	0.0170	0.820	5.80	-0.016	0.839
3-Ch-C	7.52	0.0173	0.675	3.92	-0.022	0.699
3-Ch-F	7.07	0.0187	--	NNB	-0.022	0.739

⁺NNB = NonNernstian Behavior

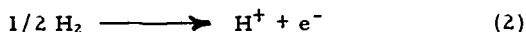
Average E₀ = 0.771 v vs NHE

Current Density (ma/cm²) at 0.3 v Polarization and Bubble Pressure

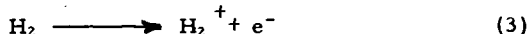
	H ₂	O ₂
1-Ch-C	4.6	17.5
1-Ch-F	5.2	4.5
2-Ch-C	4.5	6.0
2-Ch-F	6.2	--
3-Ch-C	5.2	4.8
3-Ch-F	4.7	6.8

It will be noted that the finer materials (increasing sample number corresponds to increasing fineness) give higher oxygen electrode current densities at lower polarization in the non-wetproofed condition. The hydrogen electrode showed little correlation with respect to electrochemical performance and fineness of the electrode material. Generally, higher current densities at lower polarizations are obtained for non-wetproofed materials for both the hydrogen and oxygen electrodes. This indicates that there is an inhibiting effect caused by the wetproofing agent on charcoal materials similar to the effect described for electrodes made from other fillers. The effect would be expected to be greater for the charcoal filler materials than for the standard filler materials in that the untreated materials are very hydrophillic. When these easily wet materials are treated with the paraffin in the wetproofing process it would be expected that great changes would be produced in electrochemical performance. However, the open circuit voltages of these charcoal based materials give a reverse response to wetproofing compared to the other materials in this study. Usually, non-wetproofed materials have higher open circuit voltages than wetproofed materials. In the case of charcoal based electrodes, wetproofed samples gave superior performance for both the hydrogen and oxygen electrodes.

While both the hydrogen (anode) and oxygen (cathode) electrodes showed definite bubble pressures which varied with the particular electrode material, only the oxygen electrode showed a large variation in open circuit potential with gas pressure. The variation in O. C. V. of the hydrogen electrode was in the order of 5 millivolts or less for hundred fold changes in pressure. This is probably because the reaction at the hydrogen electrode is a simple one electron change given by

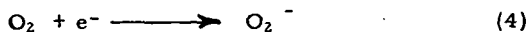


or if the molecule is considered to react in a step wise fashion then

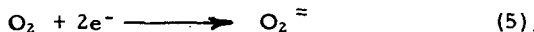


The existence of H_2^+ is considered to be very transitory (16, 17) so that the possibility of a long half-life can be discounted. Gaseous hydrogen also has a rate of diffusion some four times greater than oxygen and is considerably more soluble in an aqueous electrolyte of low pH than is oxygen.

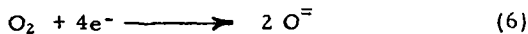
Oxygen, on the other hand, has the possibility of undergoing several reactions at the cathode, all of which vary in the electron change per mole of oxygen. Under the proper conditions one mole of oxygen can add one electron to form the perhydroxyl ion as shown by



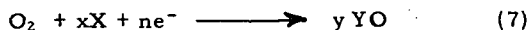
Oxygen can also add two electrons to form the doubly charged peroxide ion



And, finally, oxygen can add four electrons to form the oxide ion



A general reaction can be written to cover all three cases which takes the form



in which n is the electron change, X is a species such as C , Pt or H^+ present in the system and YO is either a surface carbon-oxygen complex or some compound with Pt (i.e., PtO , PtO_2) or H^+ (i.e., HO_2 , H_2O_2 , HO_2^- , or H_2O). Substituting the factors of equation (7) into the Nernst equation one obtains

$$E = E'_O + \frac{RT}{nF} \ln \left[\frac{a_X^x P_{O_2}}{a_Y^y O} \right] \quad (8)$$

in which "a" signifies the activity of the various reactants and products, P_{O_2} is the pressure in atmospheres of gaseous oxygen and the other symbols have their usual electrochemical significance. If only the pressure of oxygen (P_{O_2}) is varied then a_X^x and a_Y^y become constant and E'_O will equal E_O , the standard electrode potential. Substituting the numerical values for the constants in equation (8) and reducing to \log_{10} the equation becomes

$$E = E_O + \frac{0.059}{n} \log P_{O_2} \quad (9)$$

at 298.16°K. A plot of the observed potential versus the \log of P_{O_2} should yield a straight line with a slope equal to $n/0.059$. Further, at P_{O_2} equal to 1 atmosphere it is seen that E equals E_O . Such a plot for a typical electrode is shown in Figure 1. Thus, it should be possible to obtain an indication as to which of the reactions given in equations (4), (5) and (6) may be occurring at the cathodic reaction interface. Such an approach has been used recently in a study of the rest potentials of the oxygen-platinum-acid system (18).

A tabulation of the Δn values calculated using the above technique is given in Tables III, IV, V, VI along with other electrochemical observations. Some of the carbons tested gave a non-Nernstian behavior pattern (i.e., $\log P_{O_2}$ versus E observed lines not linear) and these materials are marked "NNB" under the Δn heading. For those samples that have been wetproofed (Table III), it is noted that when the coarser side of the carbon body is facing the aqueous electrolyte the Δn value is predominantly in the 3 to 4 electron region. This is an indication that the reaction occurring at the gas-electrode-aqueous interface (i.e., the reaction interface) is due to the reduction of oxygen directly to the dinegative state (i.e., an oxide ion). On the finer side, however, the electron change is in the 1 to 2 region indicating formation of perhydroxyl (O_2^-), peroxide (O_2^{2-}) or hydroperoxide (HO_2^-) at the reaction interface. For the non-wetproofed materials it is apparent that the predominant electron change is in the 1 to 2 range indicating the formation of perhydroxyl or more probably hydroperoxide intermediates at the pH values employed in this study. There appears to be no rigorous relationship between limiting pore radii, or bubble pressure, and the Δn values in the materials under study. The average E_O value is 0.832 ± 0.059 v vs the N.H.E. Using data from a standard source of electrode potentials (19) it is seen that this value does not correspond to the formation of HO_2 , H_2O_2 , or H_2O . The average E_O , as well as the individual values, do, however, fall well within the range of the listed values for the formation of some substituted quinones. The formation of such a species on the surface of a carbon body is quite possible as their presence has been determined on certain carbons by polarographic (20) and spectrophotometric (21) techniques. The fact that the E_O values have a wide variation indicates the influence of various functional groups, in different positions relative to the quinone groups, on the standard potential.

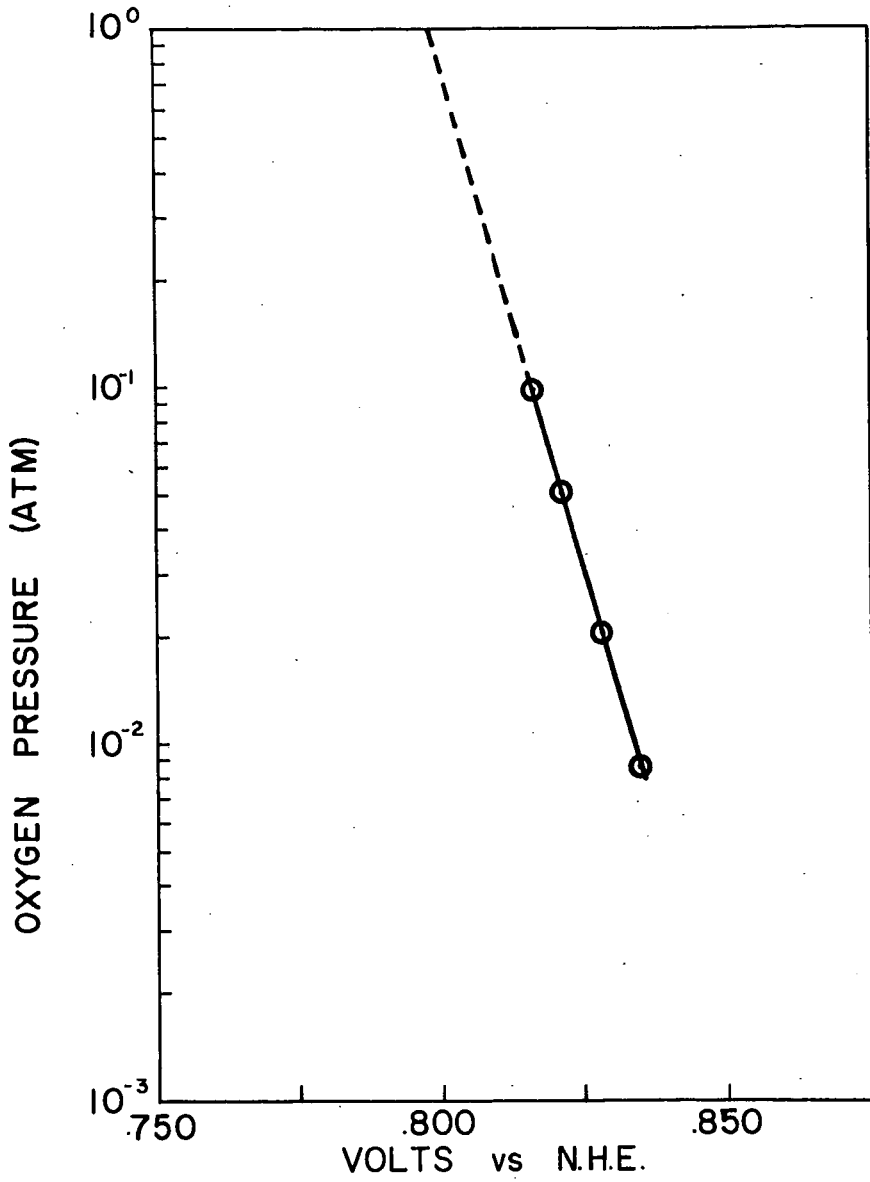


FIGURE 1

LOG O_2 PRESSURE VS. OBSERVED POTENTIAL
SAMPLE I-C-WP (536-29-I)

When platinum black is incorporated into the electrode materials during the fabricating process the electron change values appear to be radically different. In these materials the reaction at the interface seems to proceed directly to the oxide ion rather than through the intermediate, less negative, perradical as shown in Table IV. The E_0 value for electrodes containing platinum black is 0.991 ± 0.054 v vs the N. H. E., a good indication that a different reaction is occurring since the value is quite different from that found for similar materials catalyzed in the standard manner. For the quinone-hydroquinone system, higher E_0 values indicate more highly substituted aromatic structures similar to those which could be expected on a carbon surface.

The use of charcoal as a filler material results in electron change values which depend, to a degree, on the pore size of the electrode. The data for samples with coarser pores indicates reduction of the oxygen to a peroxide or hydroperoxide stage. The average E_0 obtained for these materials is 0.711 ± 0.063 v vs the N. H. E. indicating the presence of less complicated aromatic ring structures (19) on the surface. The calculated limiting pore radii of these materials vary only slightly from one material to another, even though the expected change is a twenty-fold variation. This effect could be caused by the fact that these materials are readily wet by the electrolyte as shown by their extremely low contact angles.

The wide range in E_0 values obtained could well be due to the nature of the porous electrode material. In comparison with solid, impermeable electrode materials, porous electrodes possess a larger (by orders of magnitude) contact area per unit volume of electrolyte, reactant and electrode. Because of this there can be a range of reactions, occurring at different reaction rates, within the pores. The distribution of these reactions and the predominance of one or more of these will be a function of the physical structure of the electrode matrix as well as the environment in which the electrode material is placed (22, 23). Also, because of the porous nature of the electrode material, concentrations of reacting species are constant only at the instant the circuit is closed (i. e., commencement of current flow) so that reaction distributions can be quite non-uniform within the electrode matrix. Thus linear polarization may occur only at very low overpotentials where the electrode reaction is initiated. As the reaction interface proceeds further into the matrix of the electrode, the predominating electrode reaction becomes less uniform in its distribution and more complex in its nature. The wide variation in electron change values, Δn , can be considered as evidence for the complexity of the reactions at the reaction interface on a "carbon surface". The Δn and E_0 values listed in Tables III, IV, V and VI are most probably those for the rate controlling step at the reaction interface so that it is quite probable that some carbons have surface properties which enhance the formation of one quinone intermediate over another. On a given carbon the formation of a simple quinone group,

$O = \overset{\text{C}}{\text{C}} = \overset{\text{C}}{\text{C}} = O$, may occur. On a second carbon, or at another reaction site

on the same carbon, the formation of a degenerate quinone grouping such as $\overset{\text{C}}{\text{C}} = \overset{\text{C}}{\text{C}} - O - O - \overset{\text{C}}{\text{C}} = \overset{\text{C}}{\text{C}}$ could be favored prior to a rearrangement to the quinone grouping. Considerably more experimental work is needed before a firmly supported mechanism can be postulated.

No attempt was made to interpret the electrochemical data in terms of Tafel slopes (17) derived from activation polarization data since linear polarizations were obtained only at very low overpotentials, at the initiation of the electrode reaction, due to the heterogeneous nature of a porous electrode. In addition, other investigators have also reported (24) that fuel cell systems do not yield linear polarization curves.

CONCLUSIONS

The electroreduction of oxygen at a porous carbon cathode in 3.0 N sulfuric acid in a fuel cell system appears to proceed through a quinone-hydroquinone reaction based on the comparison of measured potentials with standard potentials. The initial step in the reduction of oxygen may proceed via a one electron change to hydroperoxyl (HO_2), a two electron change to peroxide (H_2O_2) or hydroperoxide (HO_2^-) or a four electron change to water (H_2O) depending on the particular carbon material serving as the electrode. When the electrode material has been wetproofed the reduction is directly to the oxide ($\Delta n \sim 4$) state when the coarser side faces the electrolyte and to either the perhydroxyl or hydroperoxide ($\Delta n \sim 1$ or 2) when the finer zone is facing the electrolyte.

For non-wetproofed materials the electron change is apparently a function of the particular electrode surface facing the aqueous electrolyte, perhaps indicating the relative ease of formation of one substituted quinone-hydroquinone group versus another. No direct correlation between pore size distribution and electron change values is apparent. Generally, however, zones of finer porosity tend to give higher Δn values than coarser zones when a platinum black catalyst has been fabricated into the electrode material. This could be due, in part, to the increased resistance offered by the electrode matrix to diffusion resulting in more complete oxygen reaction.

The limiting pore radii of the graded porosity electrodes were calculated in order to define the position of the reaction interface within the electrode matrix. When the materials had been wetproofed by the addition of paraffin it was shown that the reaction interface was probably in the same location regardless which porosity zone faces the electrolyte. This could be explained on the basis that the wetproofing process plugged the smaller pores in the electrode, producing an electrode material without a porosity gradient. For non-wetproofed materials, the limiting pore radii showed that the reaction interface was located closer to the zone facing the electrolyte. This is an indication that the aqueous electrolyte does not penetrate the electrode matrix as deeply as the gas in the graded porosity materials. There was no correlation of electron change and/or extrapolated standard potential with the calculated limiting pore radii. When hardwood charcoal was substituted for petroleum coke as a filler material, the extrapolated standard potential indicates that a less substituted quinone-hydroquinone system may be present at the surface. Since the limiting pore radii for these materials were not appreciably different from the petroleum coke materials, it appears that material differences are the principle contributory factors to this effect.

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